



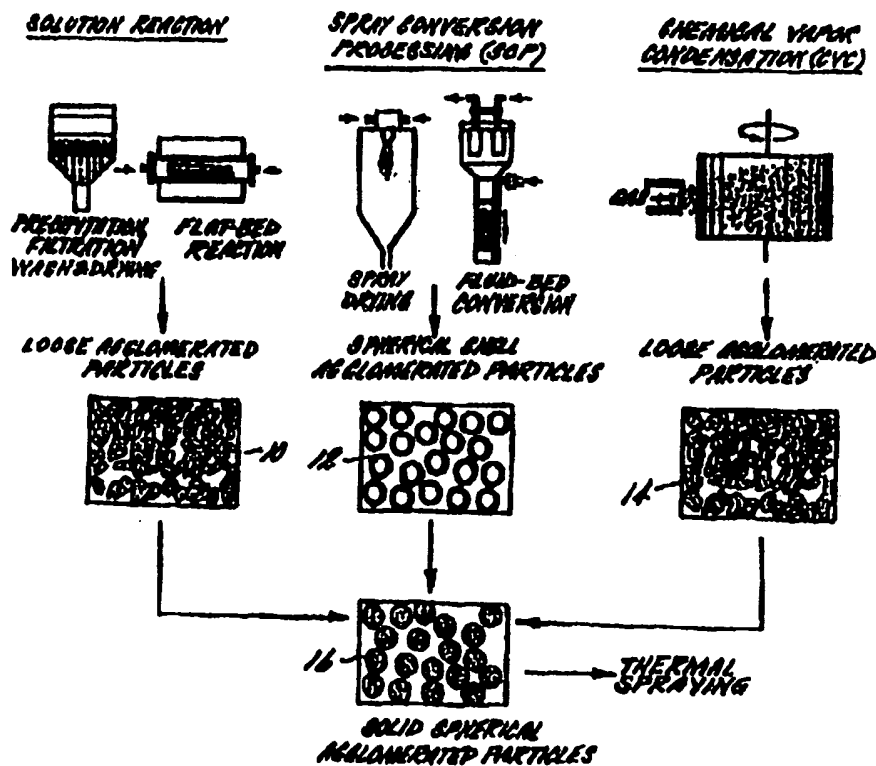
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 4/10, B05D 1/02, 1/08, 1/10, 7/00, B06B 1/20, B29B 9/08, B32B 9/00, 18/00		A1	(11) International Publication Number: WO 97/18341
			(43) International Publication Date: 22 May 1997 (22.05.97)
(21) International Application Number: PCT/US96/18467		(81) Designated States: CA, CN, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 13 November 1996 (13.11.96)		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(30) Priority Data: 08/558,133 13 November 1995 (13.11.95) US			
(71) Applicants: THE UNIVERSITY OF CONNECTICUT [US/US]; Storrs, CT 06268 (US). RUTGERS, THE STATE UNIVERSITY OF NEW JERSEY [US/US]; Piscataway, NJ 08855 (US).			
(72) Inventors: STRUTT, Peter, R.; The University of Connecticut, Longley Building, Route 44, Storrs, CT 06269 (US). KEAR, Bernard, H.; Rutgers University, 675 Brett & Bowser Road, P.O. Box 909, Piscataway, NJ 08854-0909 (US). BOLAND, Ross, F.; 316 Fern Road, West Hartford, CT 06119 (US).			
(74) Agent: MURPHY, Keith, J.; Fishman, Dionne & Cantor, 88 Day Hill Road, Windsor, CT 06095 (US).			

(54) Title: NANOSTRUCTURED FEEDS FOR THERMAL SPRAY

(57) Abstract

This invention relates to methods whereby reprocessed nanoparticle powder feeds, nanoparticle liquid suspensions, and metalorganic liquids are used in conventional thermal spray deposition to form nanostructured coatings. In one embodiment, the nanostructured feeds consist of spherical agglomerates (16) produced by reprocessing as-synthesized nanostructured powders (10, 12, 14). In another embodiment, a fine dispersion of nanoparticles is directly injected into a combustion flame or plasma thermal spray device to form nanostructured coatings. In another embodiment, liquid metalorganic chemical precursors are directly injected into the combustion flame of a plasma thermal spray device, whereby nanoparticle synthesis, melting and quenching are performed in a single operation. In these methods, ultrasound is used for disintegration of the as-synthesized particle agglomerates (10, 12, 14), nanoparticle dispersion in liquid media and liquid precursor atomization.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

NANOSTRUCTURED FEEDS FOR THERMAL SPRAY

Background of the Invention:

1. Field of the Invention

This invention relates generally to the field of nanostructured materials. In particular, this invention relates to nanostructured feeds used in the deposition of high-quality nanostructured coatings via the thermal spraying process.

2. Brief Description of the Prior Art

Materials with fine-scale microstructures have long been recognized to exhibit technologically attractive properties. In the past few years, a new class of sub-microstructured materials has been identified, composed of ultra fine grains or particles. These materials have been referred to as "nanostructured materials." Nanostructured materials are characterized by having a high fraction of the material's atoms residing at grain or particle boundaries. For example, with a grain size in the five nanometer range, about one-half of the atoms in a nanocrystalline or a nanophase solid reside at grain or particle interfaces.

Although research in the field of nanostructured materials currently focuses on synthesis and processing of nanostructured bulk materials, there is a growing interest in nanostructured coatings, including thermal barrier, hard and superhard coatings. Nanostructured bulk materials with designed multifunctional coatings present

unprecedented opportunities for advances in materials properties and performance for a broad range of structural applications.

Research on nanostructured materials has been a major activity at Rutgers University and the University of Connecticut since the late 1980's. Progress has been made in the synthesis of (1) nanostructured metal powders by the organic solution reaction (OSR) and aqueous solution reaction (ASR) method, (2) nanostructured ceramic-metal (cermet) powders by the spray conversion processing (SCP) method, and (3) nanostructured powders by the gas condensation processing method. Advances have also been made in the consolidation of nanostructured powders by solid and liquid phase sintering methods (for bulk materials) while preserving the desirable nanostructures.

There are three different methods currently in use for the synthesis of nanostructured powders, including (1) the organic solution reaction (OSR) and aqueous solution reaction (ASR) methods for synthesizing nanostructured metal powders, for example, nanostructured $\text{Cr}_3\text{C}_2/\text{Ni}$ powders; (2) the spray conversion processing (SCP) method for synthesizing nanostructured cermet powders, for example, tungsten-carbon/cobalt and $\text{Fe}_3\text{Mo}_3\text{C}/\text{Fe}$ powders; and (3) the gas condensation processing (GCP) method for synthesizing nanostructured ceramic powders, for example, titanium dioxide, zirconium dioxide and silicon/carbon/nitrogen.

The OSR and ASR methods for the preparation of nanostructured metals and alloys use three steps: (1) preparation of an organic or aqueous solution of mixed metal chlorides; (2) reductive decomposition of the starting solution with a metal hydride to obtain a colloidal solution of the metallic constituents; and (3) filtering, washing and drying, followed by gas-phase carburization under controlled carbon and oxygen activity conditions to form the desired nanodispersion of carbide phases in a metallic matrix phase.

This procedure has been used to synthesize a variety of nanostructured metal/carbide powders, including nanostructured $\text{Cr}_3\text{C}_2/\text{NiCr}$ powders for use in thermal spraying of corrosion resistant hard coatings. A small amount of an organic passivation agent, such as a solution of paraffin in hexane added to the final wash provides protection of the high surface area powder against spontaneous combustion when dried and exposed to air. The as-synthesized powders thus produced are loosely agglomerated. As used herein, the term agglomerated also encompasses aggregated particles.

The SCP method for synthesizing nanostructured cermet composite powders involves three sequential steps: (1) preparation of an aqueous solution mixture of salts of constituent elements; (2) spray drying of the starting solution to form a homogeneous precursor powder; and (3) fluid bed conversion (reduction and carburization) of the precursor powder to the desired nanostructured cermet powder. The SCP method has been utilized to prepare nanostructured WC/Co, nanostructured $\text{Fe}_3\text{Mo}_3\text{C}/\text{Fe}$ and similar cermet materials. The particles may be in the form of hollow spherical shells. The powders are usually passivated after synthesis in order to avoid excessive oxidation when exposed to air.

The GCP method is the most versatile process in use today for synthesizing experimental quantities of nanostructured metal and ceramic powders. A feature of the process is its ability to generate loosely agglomerated nanostructured powders, which are sinterable at relatively low temperatures.

In the inert gas condensation (IGC) version of the GCP method, an evaporative source is used to generate the powder particles, which are convectively transported to and collected on a cold substrate. The nanoparticles develop in a thermalizing zone just above the evaporative source, due to interactions between the hot vapor species and the much colder inert gas atoms (typically 1-20 mbar pressure) in the chamber. Ceramic powders are usually produced by a two-stage process: evaporation of a metal source, or preferably a metal suboxide of high vapor pressure, followed by slow oxidation to develop the desired nanostructured ceramic powder particles.

In the chemical vapor condensation (CVC) version of the GCP method, a hot-wall tubular reactor is used to decompose a precursor/carrier gas to form a continuous stream of clusters or nanoparticles exiting the reactor tube. Critical to the success of CVC processing are: (1) a low concentration of precursor in the carrier gas; (2) rapid expansion of the gas stream through the uniformly heated tubular reactor; (3) rapid quenching of the gas phase nucleated clusters or nanoparticles as they exit from the reactor tube; and (4) a low pressure in the reaction chamber.

The resulting nanostructured ceramic powder particles are loosely agglomerated, as in the IGC method, and display low temperature sinterability. This is in contrast to the ultra fine powders produced by conventional ambient pressure combustion flame and arc-

plasma powder processing methods, which yield cemented aggregates that can be consolidated only at much higher sintering temperatures. The CVC method has been used to synthesize nanostructured powders of a variety of ceramic materials, which cannot easily be produced by the IGC process, because of their high melting points and/or low vapor pressures. Examples are nanostructured SiC_xN_y powders, for which there are many suitable metalorganic precursors, such as hexamethyldisilazane (HMDS). The actual composition of the resulting powder is strongly influenced by the choice of carrier gas. Thus, HMDS/ H_2O , HMDS/ H_2 and HMDS/ NH_3 give nanostructured ceramic powders with compositions close to SiO_2 , SiC and Si_3N_4 , respectively.

In current industrial practice, the powders used to deposit metal, ceramic or composite coatings by thermal spray or plasma deposition consist of particles in the range from 5 to 50 microns in diameter. During the short residence time in the flame or plasma, the particles are rapidly heated to form a spray of partially or completely melted droplets. The large impact forces created as these particles arrive at the substrate surface promote strong particle-substrate adhesion and the formation of a dense coating of almost any desired material, with the coatings ranging in thickness from 25 microns to several millimeters, and formed at relatively high deposition rates.

Generally, the conventional powders used in thermal spray coating are produced by a series of steps, involving ball milling, mechanical blending, high temperature reaction, and occasionally spray drying using a binder. Powder delivery systems in thermal spray technology are designed to work with powder agglomerates with particle size in the range from 5 to 25 microns. The minimum size of the constituent grains or particles in conventional powders is in the range of 1 to 0.5 microns. In contrast, in nanostructured materials, the size of the constituent grains or particles is in the range from 1 to 100 nanometers. As-synthesized nanoparticle powders are thus generally unsuitable for conventional thermal spray coating, and need to be reprocessed in order to satisfy the size requirements of conventional spray technology. Accordingly, there remains a need for methods of re-processing as-synthesized powders so that they are suitable for conventional commercial spray deposition. Alternatively, there remains a need for allowing reliable,

inexpensive high-throughput direct injection of an as-synthesized powder, or chemical precursor for in-situ particle synthesis into the thermal spray apparatus in order to achieve reproducible, high-quality deposition of nanostructured coatings.

Summary of the Invention:

5 The above-discussed and other problems and deficiencies of the prior art are overcome or alleviated by the methods of the present invention, which for the first time allow the production of nanoparticle feeds suitable for use with conventional thermal spray technology.

10 Accordingly, in one embodiment of the present invention, there is provided a method for reprocessing as-synthesized nanoparticle powders to an aggregated form suitable for conventional spray deposition of nanostructured coatings, wherein the as-synthesized powders are first dispersed in a liquid medium by means of ultrasound, then spray dried. These spray dried agglomerated nanostructured powders have a spherical shape and narrow particle size distribution in the optimal 10-50 micron range. These
15 powders therefore have superior feed characteristics in thermal spraying and also experience uniform melting behavior in the combustion flame or plasma. As a consequence, the coatings display uniform nanostructures, negligible porosity, good substrate adhesion and excellent wear properties. In contrast to powders mixed by ball milling or mechanical blending, for example, the method of this invention allows mixing of
20 the material's constituent elements at a molecular level.

 In an alternative embodiment of the present invention, there is provided a method for direct nanoparticle injection of as-synthesized powders into the combustion flame or plasma of a conventional thermal spray deposition device, wherein the as-synthesized powders are first dispersed in a liquid medium by means of ultrasound. Direct injection by
25 this method allows reproducible deposition of high-quality nanostructured coatings without an intermediate re-processing step. The very short diffusion distance allows fast reactions to occur between nanoparticles and the vapor species in the gas stream, for example, carburization, nitridation, and boridization. This embodiment also allows the constituents of a given material to be mixed at a molecular level.

In yet another embodiment of the present invention, there is provided a method for the manufacture of nanostructured coatings using a metalorganic aerosol feedstock generated ultrasonically, wherein nanoparticle synthesis, melting and quenching are performed in a single operation.

5 The above-mentioned and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings

Brief Description of the Drawings

10 Referring now to the drawings wherein like elements are numbered alike in the several FIGURES:

FIGURE 1 is a flow diagram of the examples of the synthesis of agglomerated nanostructured powders for use in thermal spray coating, including the method of the present invention for reprocessing as-synthesized powders;

15 FIGURE 2 is a detailed flow diagram of the method of the present invention for reprocessing as-synthesized nanostructured powders;

FIGURE 3 is a scanning electron micrograph of a WC/Co nanostructured powder produced by the reprocessing method of the present invention.

20 FIGURES 4A and 4B are diagrams comparing thermal spraying of conventional cermet powder particles and agglomerated cermet powder particles of the present invention;

FIGURE 5 is a depiction of the method of the present invention for the manufacture of nanostructured coatings using a metalorganic aerosol feedstock generated ultrasonically.

Description of the Preferred Embodiment:

25 Referring now to FIGURES 1 and 2, in one embodiment of the present invention, there is provided a method for reprocessing nanoparticle powders to an agglomerated form suitable for thermal spray deposition of nanostructured coatings. According to this method, as-synthesized nanostructured powders 10, 12 and 14 are ultrasonically disintegrated and dispersed in a liquid medium, and then spray-dried to form spherical nanoparticle
30 agglomerates 16 suitable for thermal spray deposition. The original particles, typically less

than 50 microns, can be reduced to submicron dimensions, forming a viscous slurry or a colloidal suspension within minutes. While nanoparticles 10 synthesized via the solution reaction (OSR or ASR) method, nanoparticles 12 synthesized via the SCP method, or nanoparticles 14 synthesized via the CVC method are each suitable for reprocessing by the method of the present invention, it is to be understood that nanoparticles synthesized by any method are suitable for use in the present invention. In addition, while the agglomerated nanoparticle powders are particularly useful for thermal spray deposition, they may also find utility in other applications requiring agglomerated nanoparticles.

In the practice of the method of this embodiment, an as-synthesized powder which may comprise the particles 10, 12, 14 or a mixture thereof is first suspended in a liquid medium to form suspension 18. The liquid medium may be aqueous-based or organic-based, depending on the desired characteristics of the final agglomerated powder. Suitable organic solvents include, but are not limited to, toluene, kerosene, methanol, ethanol, isopropyl alcohol, acetone and the like.

The medium is then treated with ultrasound to disperse the nanostructured material, forming dispersion 20. The ultrasonic dispersal effect is most pronounced in the cavitation zone 22 at the tip of the ultrasonic horn 24. The nanostructured powder may be merely dispersed in solution, or it may form a colloidal suspension, typically within minutes.

A binder is also added to the solution, forming mixture 26. In organic-based liquid mediums, the binder comprises from about 5% to about 15% by weight, and preferably about 10% by weight of paraffin dissolved in a suitable organic solvent. Suitable organic solvents include, but are not limited to, hexane, pentane, toluene and the like. In aqueous-based liquid mediums, the binder comprises an emulsion of commercially available polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), carboxymethyl cellulose (CMC), or some other water soluble polymer, formed in de-ionized water. The binder is present in the range from about 0.5% to about 5% by weight of the total solution, and preferably from about 1% to about 10% by weight of the total solution. The preferred binder is CMC.

After mechanical mixing and if required further ultrasound treatment the suspension of nanostructured powder in the liquid medium 26 is spray-dried in hot air to form agglomerated particles 16. While any suitable non-reactive gas or mixture thereof may be used, hot nitrogen or hot argon is preferred. Because there is no requirement for

the treatment of exhaust gases from the spray drier using aqueous-based liquid mediums, these are preferred where possible.

After spraying, powders 16 are heat-treated at low temperatures ($<250^{\circ}\text{C}$) to expel residual moisture, leaving the organic component (polymer or paraffin) as a binder phase.

5 If necessary, a further heat treatment step at a high temperature effective to remove adsorbed and chemisorbed oxygen and to promote partial sintering may be added. For example, heat treatment at about 600°C is effective. The resulting powder may then be used in conventional thermal spray deposition processes. The following non-limiting examples illustrate the method of re-processing as-synthesized nanostructured powders
10 using ultrasonic dispersion.

Example 1

Typical processing conditions for preparing nanostructured WC/Co powder agglomerates are as follows. Nanostructured WC/Co, prepared by means well-known in the art, is formed into an approximately 50 wt% solution in de-ionized and deoxygenated
15 water. An ultrasonic horn, operating at a frequency of 20,000 Hertz and power of 300-400 watts, is used to disperse the nanostructured WC/Co to form a low viscosity slurry. With this energy input, original as-synthesized hollow spherical shell particles of 10-50 micron diameter are rapidly disintegrated and dispersed in the fluid medium, forming a dispersed phase of particle size of about 100 nm. Subsequently, 5-10 wt% carbon black and a 2-3%
20 by weight solution of PVP in deionized, deoxygenated water are added to the suspension. Carbon black is optionally added to compensate for the carbon loss of WC particles by high reaction in the flame or plasma. CMC is also suitable for use with WC/Co materials.

After mixing and further ultrasonic treatment, the slurry is spray-dried in a commercial unit to form a powder consisting of solid spherical particles with a mean
25 diameter in the 5-20 micron range as shown in FIGURE 3. Finally, it is preferable to clean the powders after agglomeration by a low temperature de-gassing treatment under reduced pressure prior to back filling with dry nitrogen. The powders can then be stored indefinitely in nitrogen without degradation.

Because of the high surface area of the nanostructured WC/Co powder
30 agglomerates, there is the potential for in-situ decarburization within the agglomerates, due

to the presence of oxygen or oxygen-rich species. To eliminate this problem it is preferable to introduce a passivation treatment at some stage in the powder processing using a suitable oxygen-free compound, such as paraffin. The paraffin is chemisorbed on the high surface area nanoparticles. Preferably, the paraffin is introduced in a hexane solution (5-10% by weight).

The high velocity oxy-fuel (HVOF) process is ideally suited for depositing nanostructured cermet coatings, because of the relatively low flame temperature and short particle transit time, which minimizes deleterious reactions in the flame.

A feature of using cermet nanostructured powders such as WC/Co reprocessed by the method of the present invention is the homogeneous melting of the matrix (binder) phase upon thermal spray coating, with the formation of semi-solid or "mushy" particles. Referring now to FIGURES 4A and 4B, a conventional powder particle 40 contains a hard particle phase 42 surrounded by a solid matrix phase 44. In the thermal region of the spray apparatus, the solid matrix phase 44 becomes a molten matrix phase 46. Thus, in a conventional cermet powder particle 40 the large (5-25 micron diameter) carbide grain 42 undergoes little size change in the thermal region, because of the finite time for heat transfer during the 1 millisecond transit time between exiting the gun nozzle and impact with substrate. The coatings 48 formed by these particles may therefore be porous.

In contrast, the agglomerated cermet powder particles 50 of the present invention contain hard particles 52, with a grain size in the range from about 5 to about 50 nanometers, within a matrix phase 54, agglomerated by binder 56. During thermal spraying, the small size of the carbide grains 52 of the agglomerated nanostructured particles 50 allow the particles to rapidly dissolve in the molten matrix 58 to produce a "mushy" cermet particle 60. This mushy particle 60 will readily flow upon impact with the substrate to form a highly adherent dense coating with low porosity 62. The degree of fluidity of the impacting particle can be controlled by selecting the degree of superheat above the eutectic point of the impacting particles. Additionally, a high impact velocity of the mushy nanostructured cermet particles facilitates improved spreading and adhesion to the substrate surface.

Example 2

Nanostructured $\text{Cr}_3\text{C}_2/\text{NiCr}$ powders produced by the ASR and OSR methods are in the form of loose agglomerates of variable size and morphology. Using the above general procedure, these powders can be ultrasonically dispersed in an aqueous or organic liquid medium with a polymer or paraffin binder and spray dried to form uniform-sized spherical agglomerates of 5-25 microns diameter. Moreover, during thermal spraying, the nanocomposite powders experience partial melting and undergo splat quenching when they impact the substrate surface. This behavior is similar to that described for nanostructured WC/Co powders.

Example 3

Nanostructured SiO_2 powders may be produced by combustion flame synthesis, a commercial process. The as-synthesized powder has a high surface area ($>400 \text{ m}^2/\text{gm}$), and is in the form of hard agglomerates known as "cemented aggregates," with up to 10-100 nanoparticles per aggregate. Such powders can be readily dispersed in an aqueous solution because they are inherently hydrophilic. The resulting colloidal suspension, containing PVA, PVP or CMC as a binder, can then be converted into spherical agglomerates by spray-drying, as discussed above. The behavior in thermal spraying, however, is different since the SiO_2 particles experience softening rather than melting.

The spray-dried agglomerated nanostructured powders described in the above examples have a spherical shape and narrow particle size distribution in the optimal 10-50 micron range. As such, they have superior feed characteristics in thermal spraying and also experience uniform melting behavior in the combustion flame or plasma, and the coatings formed therefrom display uniform nanostructures, negligible porosity, good substrate adhesion and excellent wear properties. In particular, coatings formed by this method from cermet materials such as WC/Co, $\text{Cr}_3\text{C}_2/\text{Ni}$, $\text{Fe}_3\text{Mo}_3\text{C}/\text{Fe}$ have novel nanostructures comprising a nanodispersion of hard carbide phase in an amorphous or nanocrystalline metal-rich matrix phase, thereby displaying superior hardness and wear resistance.

In an alternative embodiment of this invention, nanostructured powder feeds are introduced into a thermal spray system directly after ultrasound dispersion. Suitable as-

synthesized nanostructured powders for the practice of this invention are those produced by any physical method, such as GCP, or by chemical processing methods, such as the IGC and CVC methods. Such powders are monodispersed and loosely agglomerated. Particle size is easily controlled over the range 3-30 nanometer range by careful adjustments of certain critical processing parameters known in the art. These loosely agglomerated powders can be readily dispersed in de-ionized water, various alcohols or liquid hydrocarbons by ultrasonic agitation to form a colloidal suspension or slurry. This nanoparticle suspension or slurry can then be introduced, along with liquid kerosene fuel, directly into the combustion zone of an HVOF gun via the liquid feed. Alternatively, the suspension or slurry may be introduced in the form of an aerosol into the gas feed of a plasma or HVOF gun.

Characteristics of this embodiment are that the particles rapidly heat up in a short distance from the gun nozzle and almost instantaneously achieve the velocity of the gas stream, which is in the supersonic range. In some cases, the nanoparticles vaporize, prior to condensation on the cold substrate. In this case, the method becomes in effect a very high rate CVD process.

Where applicable for an individual composition, direct nanoparticle injection by this method offers a number of advantages. First, it eliminates the need for powder re-processing. Secondly, two or more nanoparticle feed systems, operating continuously or sequentially, can produce nanomultilayers or compositionally modulated structures, even down to nanoscale dimensions. Thirdly, the dispersion may be done in the same liquid used as the fuel for the thermal spray apparatus, e.g., kerosene. And finally, because of the short diffusion distances, very fast reactions occur between nanoparticles and the vapor species in the gas stream (e.g., carburization, nitridation and boridization).

The direct injection method may also be used to incorporate ceramic nanostructured whiskers, hollow shells and other particulate forms into the nanocomposite coating. Hollow ceramic microspheres (1-5 microns diameter) are available commercially. More generally, mixtures of different phases and particle morphologies may be used to generate almost any desired coating structure, including whisker-reinforced and laminated nanocomposites.

-12-

The simplicity, versatility, and scalability of the direct nanoparticles injection method thus presents opportunities to develop new classes of thermal sprayed nanostructured coatings. Moreover, because direct injection in thermal spray apparatuses can be adapted to existing thermal spray systems, it is inherently cost effective. The following non-limiting examples illustrate the method of this embodiment for injection of as-synthesized nanostructured powders directly after ultrasonic dispersion.

Example 4

Nanostructured ZrO_2 , Al_2O_3 , SiO_2 and SiC_xN_y powders produced by the CVC method, or nanostructured $Cr_3C_2/NiCr$ produced by the OSR process, are readily dispersed in organic liquid media to form colloidal suspensions, because of their ultra-fine particle size. Thus, these materials are ideal for direct injection of nanoparticles into the fluid stream of a typical thermal spray gun. High density coatings with amorphous and partially amorphous structures were produced from nanostructured SiO_2 and nanostructured $Cr_3C_2/NiCr$ powders respectively.

Example 5

Submicron nanostructured WC/Co particles can be maintained in a highly dispersed state in a liquid phase after ultrasonic treatment provided that mechanical agitation is continuously applied. Thus, it is not necessary to form completely stable colloidal suspensions with nanostructured WC/Co powders. The coatings produced by subsequent direct injection into the combustion zone of a thermal spray gun are similar to those generated using powder agglomerates as feed materials.

Example 6

The direct injection method was used to spray-deposit nanostructured yttria-stabilized zirconia (YSZ) coatings on pre-oxidized metal-CrAlY substrates. The coatings are preferentially compositionally graded to minimize thermal expansion mismatch stresses, which is a prerequisite to enhancing their resistance to spallation under thermal cycling conditions.

Example 7

A novel type of thermal barrier coating (TBC) may be produced by introducing hollow ceramic microspheres into a nanostructured YSZ overlay coating, which is supported on a metal-CrAlY bond coat. Alternatively, the ceramic microspheres may be incorporated into the metal-CrAlY bond coat. In this case, a high volume fraction of microspheres is required to ensure a high thermal impedance for the coating layer.

Example 8

When a slurry mixture of ceramic nanoparticles and hollow microspheres is introduced into a combustion flame or plasma, it is possible to selectively melt the nanoparticles while leaving the microspheres unmelted. Thus, a composite coating is developed in which the hollow ceramic spheres are bonded to the substrate by a dense nanograined ceramic coating.

Thermal barrier coatings of nanostructured YSZ may be prepared by either the re-processing method or by the direct injection method. In either case, the final coating may consist of either equiaxed or columnar grains, depending primarily on the particle deposition rate and temperature gradient in the deposited coating.

In yet another embodiment of this invention, metalorganic precursor aerosols generated by an ultrasonic nozzle serve as feedstock materials for thermal spraying processing. This offers the advantage of combining of nanoparticle synthesis, melting and quenching in a single operation. Referring now to FIGURE 5, liquid precursor 80 is introduced into ultrasonic nozzle 82. The nozzle sprays the resulting aerosol 84 into a plasma flame 86, generated by the passage of plasma gas over electrode 88, yielding nanoparticles 90, which may then be quenched on a substrate. For example, the metalorganic precursor hexamethyldisilazane (HMDS) was ultrasonically atomized in air and delivered to the exit nozzle of a DC plasma gun. Rapid pyrolysis of the precursor compound led to the formation of clusters or nanoparticles of nanostructured SiC_xN_y , which emerged as a high velocity beam from the gun. The coating formed when these hot particles impinged and coalesced on the substrate surface.

-14-

The nanostructured coatings formed by the methods of this invention find utility in a broad range of applications. In particular, nanostructured coatings formed from hydroxyapatite or vitellium are useful in medical devices. The coatings display uniform nanostructures, negligible porosity, good substrate adhesion and excellent wear properties. In contrast to powders mixed by ball milling or mechanical blending, for example, the method of this invention allows mixing of the material's constituent elements at a molecular level. The very short diffusion distance in the direct injection embodiment allows fast reactions to occur between nanoparticles and the vapor species in the gas stream, for example, carburization, nitridation, and boridization.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

What is claimed is:

-15-

CLAIM 1. A method for the production of agglomerated nanostructured particles, comprising the steps of:

- (a) dispersing a nanostructured material in a liquid medium by ultrasonic means;
- 5 (b) adding an organic binder to the medium yielding a solution; and
- (c) spray-drying the solution to form agglomerated nanostructured particles.

CLAIM 2. The method of claim 1, further comprising the step of treating the spray-dried particles to remove residual moisture.

CLAIM 3. The method of claim 1, wherein said treating step to remove residual moisture is by heat treatment.

CLAIM 4. The method of claim 1, wherein the nanostructured particles have a particle size in the range from about 5 to about 20 microns in diameter.

CLAIM 5. The method in claim 1, wherein said liquid medium is selected from a group consisting of water, toluene, kerosene, methanol, ethanol, isopropyl alcohol and acetone.

CLAIM 6. The method of claim 1, wherein the organic binders are selected from a group consisting of polyvinyl alcohols, polyvinyl pyrrolidones, and carboxymethyl cellulose.

CLAIM 7. The method of claim 6, wherein the organic binders are present in the range from about 0.5% to about 5% by weight of the total solution.

CLAIM 8. The method of claim 1, wherein the organic binder comprises a mixture of from about 5% to about 15% by the weight of the total solution of paraffin dissolved in an organic solvent.

-16-

CLAIM 9. The method of claim 1, further comprising the step of heat treatment in flowing hydrogen at high temperature to remove adsorbed or chemisorbed oxygen and to promote partial sintering.

CLAIM 10. A method for the direct injection of nanostructured particles into a thermal spray gun for thermal spray deposition, comprising the steps of:

(a) dispersing a nanostructured material in a liquid medium by means of ultrasound to form a dispersed solution;

5 (b) injecting said dispersed solution directly into a feed of a thermal spray apparatus.

CLAIM 11. The method of claim 10, wherein the dispersed solution is injected into the liquid feed of a thermal spray apparatus.

CLAIM 12. The method of claim 10, wherein the dispersed solution is injected into the gas feed of a thermal spray apparatus in the form of an aerosol.

CLAIM 13. The method of claim 10, wherein the dispersed solution further comprises particulate elements selected from the group consisting of ceramic whiskers and ceramic hollow shells, cermet whiskers and cermet hollow shells.

CLAIM 14. A nanostructured feed for thermal spray deposition formed by the method of claim 1 or claim 10.

CLAIM 15. A nanostructured feed according to claim 14, wherein the feed is derived from a nanostructured material selected from the group consisting of WC/Co, $\text{Cr}_3\text{C}_2/\text{Ni}$, $\text{Fe}_3\text{Mo}_3\text{C}/\text{Fe}$, yttria-stabilized zirconia, and SiC, Si_3N_4 , and MnO_2 .

CLAIM 16. A nanostructured feed according to claim 14, wherein the feed further comprises carbon black.

-17-

CLAIM 17. A method for producing a nanostructured coating, comprising the steps of:

(a) dispersing a nanostructured material in a liquid medium by means of ultrasound;

(b) adding an organic binder to said medium yielding a solution;

5 (c) spray-drying the solution, thereby forming agglomerated nanostructured particles; and

(d) spray coating the nanostructured particles onto an article to form a nanostructured coating.

CLAIM 18. A nanostructured coating produced by the method of claim 17, wherein the coating is formed from a cermet material and contains a nanodispersion of hard carbide phase in an amorphous metal-rich phase.

CLAIM 19. A method for producing a nanostructured coating, comprising the steps of

(a) dispersing a nanostructured powder in a liquid medium by means of ultrasound;

5 (b) injecting said dispersed solution directly into the feed of a thermal spray gun; and

(c) spray coating the nanostructured powder onto an article to form a nanostructured coating.

CLAIM 20. The method of claim 19, wherein the dispersed solution further comprises particulate elements selected from the group consisting of ceramic whiskers, ceramic hollow shells.

CLAIM 21. The method of claim 17 or claim 19, wherein the amount of superheat in the spray coating step is above the eutectic point, effectively forming mushy particles that will readily flow upon impact with the article being spray coated.

CLAIM 22. A nanostructured coating formed by the method of claim 17 or claim 19.

-18-

CLAIM 23. The nanostructured coating of claim 22 wherein the nanostructured material comprises yttria-stabilized zirconia, thereby forming a thermal barrier coating.

CLAIM 24. The nanostructured coating of claim 23 wherein the coating contains equiaxed grains.

CLAIM 25. The nanostructured coating of claim 23 wherein the coating contains columnar grains.

CLAIM 26. The nanostructured coating of claim 22 wherein the nanostructured materials comprise ceramic, cermet, and metal materials.

CLAIM 27. The nanostructured coating of claim 26, wherein the nanostructured powders are selected from the group consisting of WC/Co, $\text{Cr}_3\text{C}_2/\text{Ni}$, $\text{Fe}_3\text{Mo}_3\text{C}/\text{Fe}$, SiC, Si_3N_4 , yttria-stabilized zirconia, hydroxyapatite, vitellium and MnO_2 .

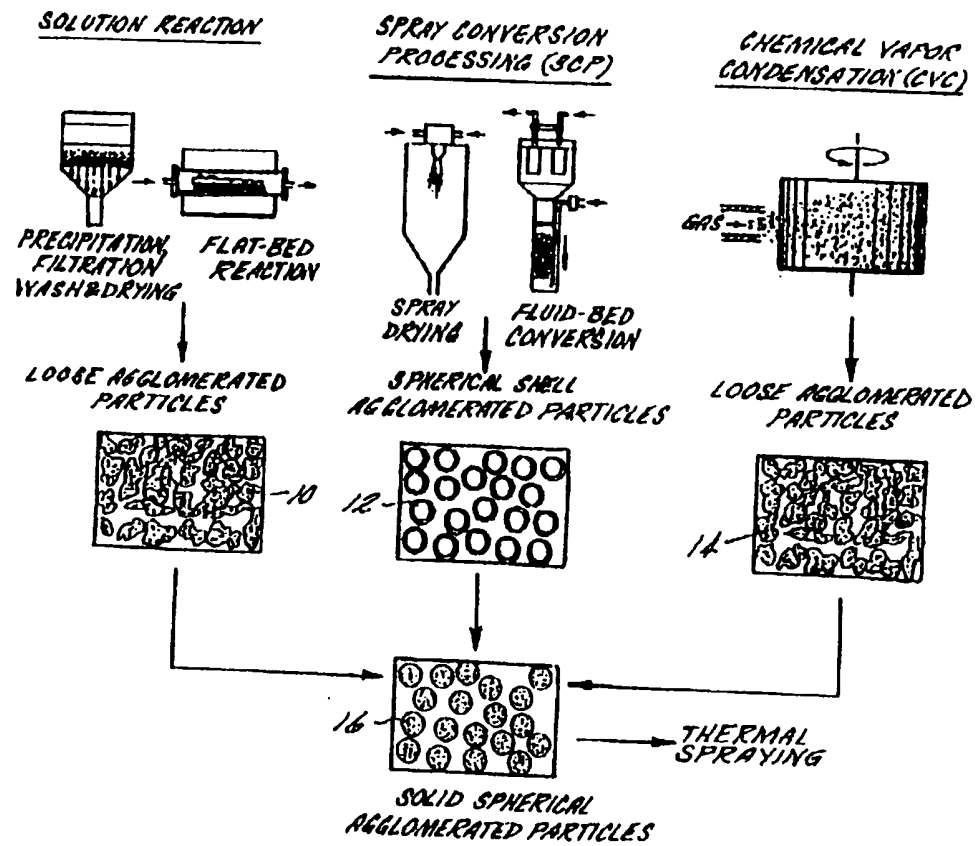
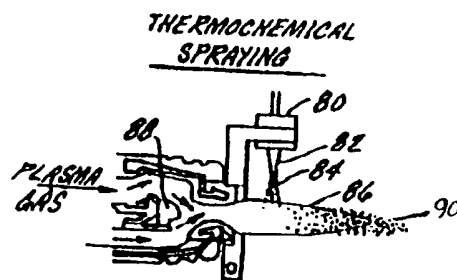
CLAIM 28. A method of forming a nanostructured coating by

- (a) forming a solution of an metalorganic feedstock;
- (b) atomizing the metalorganic solution with ultrasound; and
- (c) delivering the atomized solution to the exit nozzle of a plasma gun, where it

5 then contacts the article to be coated.

CLAIM 29. A nanostructured coating formed by the method of claim 28.

CLAIM 30. The coating of claim 29, wherein the metalorganic feedstock is hexamethyldisilazane.

FIG. 1FIG. 5

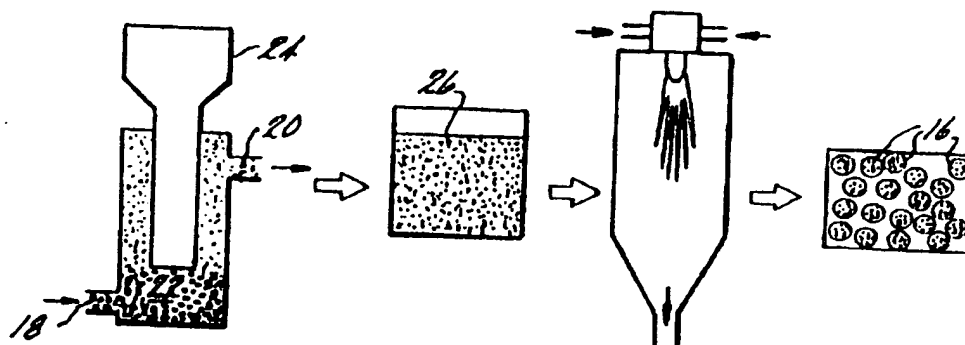
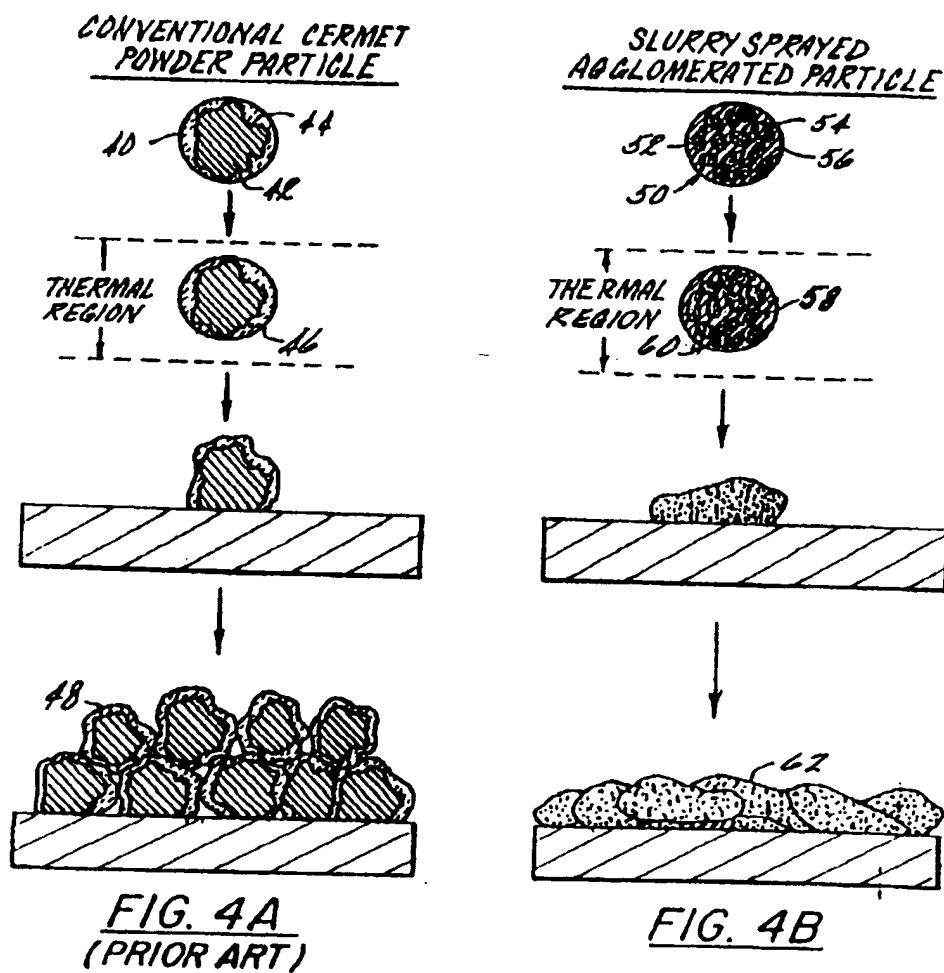
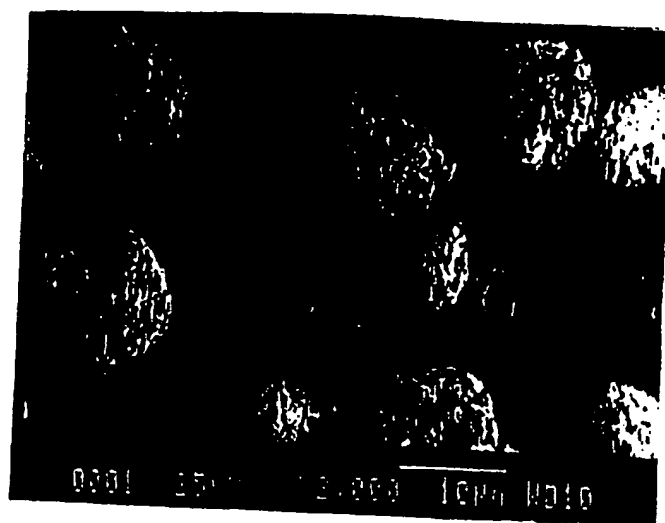
FIG. 2

FIGURE 3.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18467

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/212, 421, 422, 447, 450, 453, 569, 576, 577, 600, 601; 264/9; 428/402, 689

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,617,358 A (DITTRICH) 02 NOVEMBER 1971. See entire document.	1-30
Y	US 4,746,468 A (OZAKI et al) 24 MAY 1988. See columns 2-3.	1-30
Y	US 4,982,067 A (MARANTZ et al) 01 JANUARY 1991. Column 5, lines 50-55.	10-16, 19-30
Y	US 5,213,851 A (SNYDER et al) 25 MAY 1993. Column 7, lines 25-35 and column 8, lines 15-25.	12
Y	US 3,419,415 A (DITTRICH) 31 DECEMBER 1968. Column 3, lines 5-15.	16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" documents of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

04 FEBRUARY 1997

Date of mailing of the international search report

11 MAR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

KATHERINE A. BAREFORD

Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18467

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C23C 4/10; B05D 1/02, 1/08, 1/10, 7/00; B06B 1/20; B29B 9/08; B32B 9/00, 18/00

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

427/212, 421, 422, 447, 450, 453, 569, 576, 577, 600; 264/9; 428/402,689